Magnetic properties of the GdFeSi – GdTiSi solid solutions

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Abstract. The $GdFe_{1-x}Ti_xSi$, x=0-0.2 intermetallic compounds with a tetragonal crystal structure of the CeFeSi (*P4/nmm*)-type have been studied. It was obtained that the lattice parameter c and the Curie temperature increase quickly, whereas the lattice parameter a is almost unchanged in the system with increasing of Ti content. The GdFeSi compound is easily magnetized along the [001] axis, the field of magnetic anisotropy equals to ~3.8 kOe at T = 90 K. The saturation magnetization does not change in the $GdFe_{1-x}Ti_xSi$ system.

1. Introduction

The GdFeSi and GdTiSi intermetallic compounds crystallize in the same tetragonal CeFeSi (*P4/nmm*)-type structure. This structure is built from alternating (001) layers with the sequence: Gd-Si-T2-Si-Gd-Gd-Si-T2-Si-Gd (T = Fe, Co, Ti, Mn). This is why the exchange interactions between atoms Gd–Gd, Gd–T, T–T in GdTSi depend on the lattice parameter c. The hybridization between Si p states and T 3d states causes the filling of 3d band and, as a result, absence of the magnetic moment of Fe or Co in the GdFeSi compound [1,2]. Mn is a unique example of a 3d-transition metal T with a magnetic moment in the GdTSi compounds.

Thus, the magnetic properties of the GdTSi compounds, T = Fe, Co, Ti, Mn depend on the interatomic distances along the c axis, as well as on the number of 3d electrons. Therefore, it is interesting to study the magnetic and structural properties of solid solutions of the GdFeSi and GdTiSi compounds, in which these parameters differ significantly. The ratio (0.863) of the atomic radii of Fe (0.126 nm) and Ti (0.146 nm) is close to the critical value of the Yum-Rosery rule for the formation of solid solutions of these compounds. In addition, Fe and Ti are located in different columns of the Periodic Table and significantly differ in the number of 3d electrons: 6 and 2 in Fe and Ti atoms, respectively.

2. Experimental details

The $GdFe_{1-x}Ti_xSi$ compounds with x=0-0.2 were prepared by arc melting in an argon atmosphere. The ingots were homogenized at 1073 K for 8 days and then quenched in water. X-ray powder diffraction analysis was employed to determine the phase composition, structure type and lattice parameters under ambient conditions. A diffractometer of Empyrean Series 2 (PANalytical) and CuKα radiation were used. The HighScore v.4.x programs were used for calculation of the lattice parameters and analysis of phase compositions. The alloys crystallize in the tetragonal CeFeSi (*P4/nmm*)-type structure with some amount of Gd_5Si_3 phase. It was possible to extract single-crystalline samples of about 1-2 mg in weigh from the ingot of GdFeSi. The single-crystalline specimens were checked and oriented by the Laue X-

ray method. A vibromagnetometer 7407 VSM (Lake Shore Cryotronics) devices was used for magnetic study. The magnetization isotherms *M(H)* were recorded on single-crystalline and polycrystalline samples in a magnetic field of strength up to 1.7 T and in the temperature range 80–440 K. The saturation magnetization M_{sat} at 90 K was determined by the linear extrapolation of the high-field part of the *M(H)* curves to zero inverse internal field (1/*H*).

3. Experimental results and discussion

3.1. Crystal structure analysis

The compounds investigated crystallize into the tetragonal CeFeSi (*P4/nmm*)–type structure, the fraction of a parasitic Gd_5Si_3 phase is also presented in the alloys. The experimental and calculated X-ray diffraction patterns for $GdTi_{0.05}Fe_{0.95}Si$ are shown in Figure 1. The presence of small additional reflections from Gd_5Si_3 were taken into account in simulations. The content of the main phase in the $GdFe_{1-x}Ti_xSi$ alloys with x = 0, 0.05 equals to 92%.

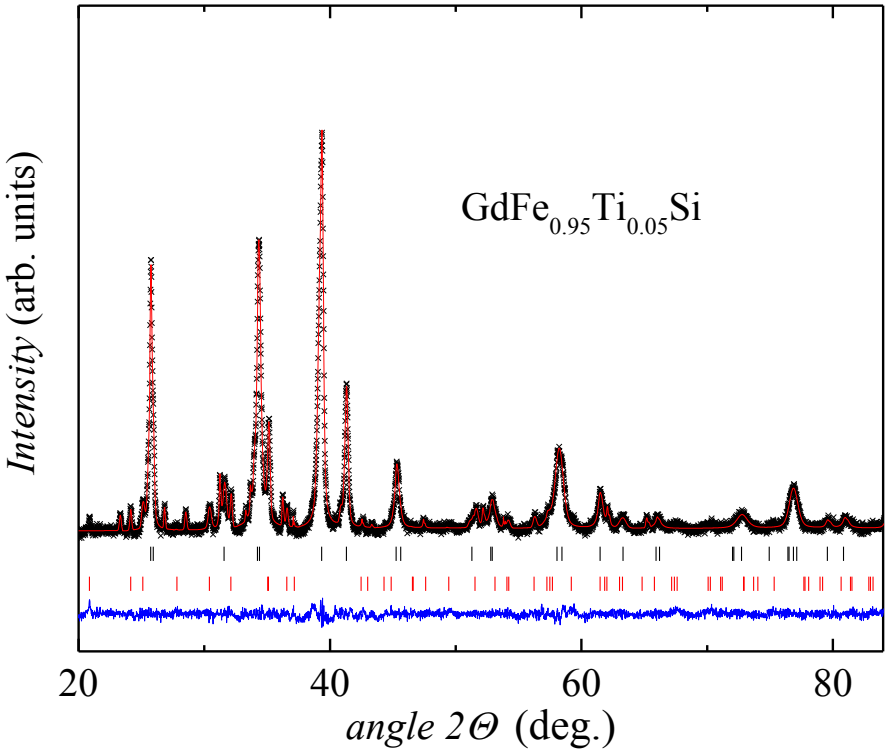

Figure 1. X-ray diffraction pattern of the $GdFe_{0.95}Ti_{0.05}Si$ compound (symbols) and its fitting (envelop curve). The lower curve is the difference between the experimental and the calculated results. Vertical lines show the reflection position for (up-down) CeFeSi and Mn_5Si_3 lattices.

As one can see in Figure 2, the increase of Ti content in the $GdFe_{1-x}Ti_xSi$ system results in an quick increase in the lattice parameter *c* for *x*=0-0.1 and then more moderate increase *c* for *x*=0.1-0.2, while the change of the parameter *a* is negligible. The increase of the lattice parameter *c* in the $GdFe_{1-x}Ti_xSi$ system is due to the large atomic radius of Ti (0.146 nm), compared with Fe (0.126 nm). The concentration dependences of the Curie temperature and the lattice parameter *c* (Figure 2) for the $GdFe_{1-x}Ti_xSi$ system are similar and indicate the limit of a solubility for the compositions x = 0.1-0.2. Thus, although the initial compounds of the $GdFe_{1-x}Ti_xSi$ system with *x*=0 и 1 have the same tetragonal CeFeSi (*P4/nmm*)–type structure, their mutual solubility is in the small range of approximately *x*=0-0.2. Apparently, the main reason for such a small solubility is in the large difference between the atomic radii of Fe and Ti, the ratio of which (0.863) is at the limit of the Yum-Rosery rule for the formation of

substitution solid solutions. The analogous small 9-10 at% Ti solubility in GdMnSi was early obtained in Ref. [3].

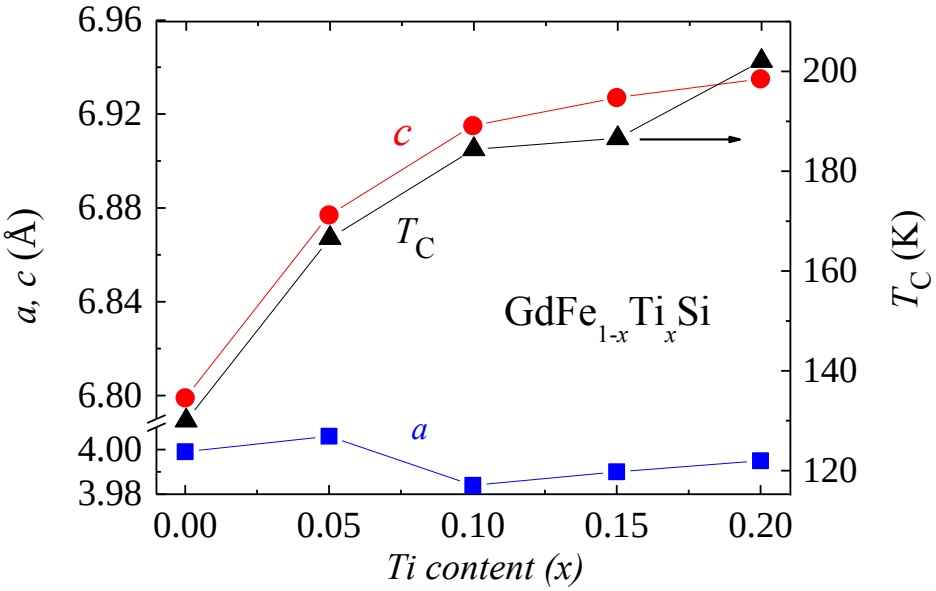

Figure 2. Dependences of the lattice parameters *a* (■), *c* (●) and the Curie temperature T_C (▲) of the $GdFe_{1-x}Ti_xSi$ compounds versus Ti content.

3.2. Magnetic properties

Curie temperature were determined with the help of Arrot-Belov plots [3] as is shown for $GdFe_{0.95}Ti_{0.05}Si$ in Figure 3. The positive slopes of the curves indicate that the FM-PM transition can be classified as second order type phase transition according to the Ehrenfest [1].

The approximate constancy of the lattice parameter *a* means the invariance of the interatomic distance T–T in the basal plane. The Gd-Gd and Gd-Fe interatomic distances in the $GdFe_{1-x}Ti_xSi$ system increase because of the increase of the lattice parameter *c* when Ti substitutes for Fe. As a result, the Curie temperature T_C should decrease. On the contrary, there is a significant increase in T_C (Figure 2) that can be explained by assuming the itinerant magnetism of these compounds. In fact, the 3*d* band is filled in GdFeSi. The replacement of Fe by Ti in GdFeSi leads to a sharp decrease in the number of 3*d* electrons "spin-down", since Fe and Ti atoms significantly differ in the number of 3*d* electrons: 6 and 2, respectively. As a result, the number of 3*d* electrons with "spin up", not compensated by 3*d* electrons with "spin down", increases. Owing to this, indirect exchange interactions between the Gd ions become stronger, because they are realized through the polarization of conduction electrons. Thus, the polarization of delocalized 3*d* electrons by the exchange interactions between Gd atoms prevails over the increase of interatomic distances Gd-Gd and Gd-Fe in the $GdFe_{1-x}Ti_xSi$ compounds for change of the Curie temperature.

The magnetization curves versus internal field for the GdFeSi single crystal measured along the three main crystallographic directions [100], [010] and [001] at T = 90 K are presented in Figure 4. The direction of easy magnetization lies along the [001] axis. There is no magnetic anisotropy in the "hard magnetized" basal plane. The anisotropy field equals ~3.8 kOe which is close to the value ~4 kOe at T = 78 K in Ref. [5]. This small value of the magnetic anisotropy field in GdFeSi is explained by spherical symmetry of 4*f*-shells of Gd ions and non-magnetic state of Fe and Si ions.

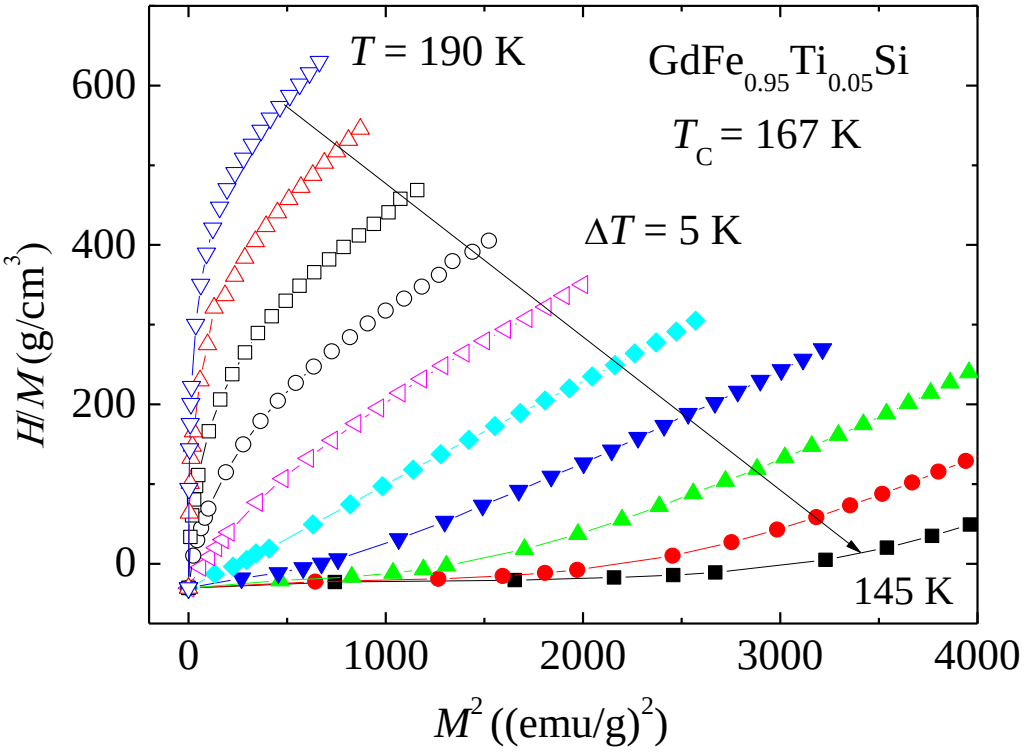

Figure 3. Arrot plots for the $GdFe_{0.95}Ti_{0.05}Si$ compound.

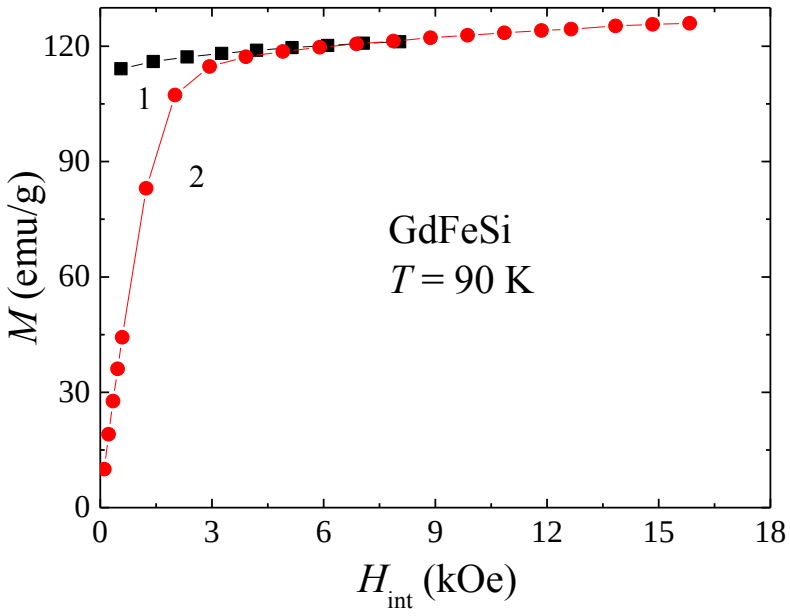

Figure 4. Magnetization curves versus internal field H_{int} measured along the crystallographic directions [001] (1), [100] (2) or [010] (2) of the GdFeSi single crystal at $T = 90$ K.

The saturation magnetization $M_{sat.}$ at 90 K of the $GdFe_{1-x}Ti_xSi$, x=0-0.2 compounds is about the same and equals to ~5.6 μ_B/f.u. for GdFeSi. This result does not contradict the fact that Fe and Ti ions do not carry a magnetic moment in the initial ternary compounds.

The isothermal magnetic entropy change $-\Delta S_M$ (i.e. the magnetocaloric effect MCE) was calculated from the magnetization isotherms $M(H)$ using the well-known Maxwell relation [1,2]:

$$-\Delta S_M(T,H) = \int_0^H (\partial M / \partial T)_H dH \quad (1)$$

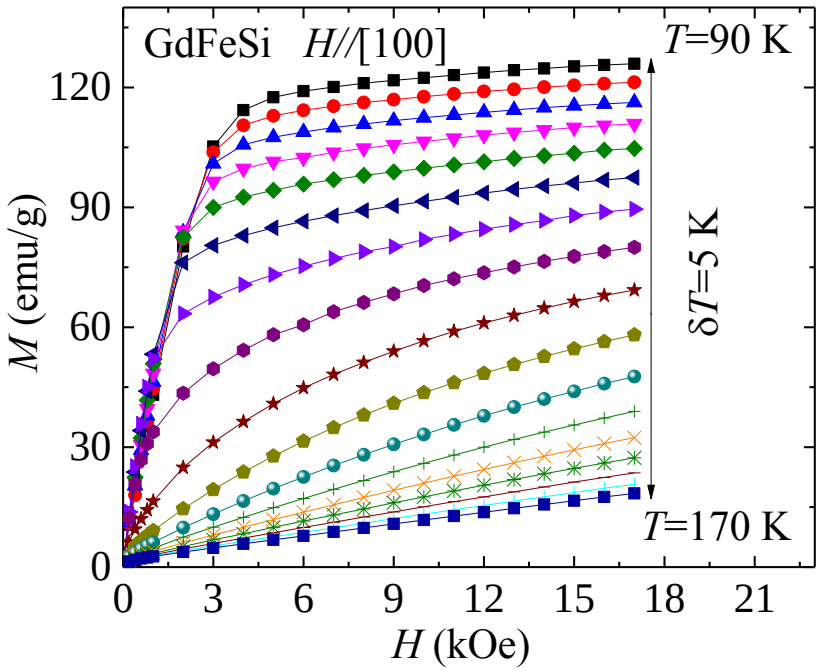

Figure 5. Magnetization isotherms *M(H)* measured along the *a*-axis of GdFeSi in the range T=90-170 K (up-down). The temperature step is 5 K.

Typical magnetization isotherms measured along the *a*-axis of the GdFeSi single crystal are shown in Figure 5. The maximum $-\Delta S_M(T)$ value for the GdFeSi compound is 5.0 J/kg*K in a 17 kOe field. This is close to the value of 6 J/kg*K in a field of 20 kOe in Ref. [2]. For $GdFe_{0.95}Ti_{0.05}Si$, the $-\Delta S_M(T)$ value is half as much as for GdFeSi. Since their saturation magnetizations are the same, this sharp drop of the MCE is most likely caused by the heterogeneity of the $GdFe_{0.95}Ti_{0.05}Si$ substitution alloy.

4. Conclusions

The $GdFe_{1-x}Ti_xSi$, x=0-0.2 intermetallic compounds with a tetragonal crystal structure of the CeFeSi (*P4/nmm*)-type have been studied. It was obtained that the lattice parameter c and the Curie temperature T_C increase, whereas the parameter a is almost unchanged in the system when the content of Ti increases. Because the increase of the interatomic distances should lead to a decrease of T_C, one can conclude that the observed increase of T_C is stipulated by a decrease of number of 3*d* electrons due to the substitution of Fe by Ti. The GdFeSi compound is easily magnetized along the [001] axis, the field of magnetic anisotropy equals to ~3.8 kOe at T = 90 K. The saturation magnetization does not change in the $GdFe_{1-x}Ti_xSi$ system. The maximum $-\Delta S_M(T)$ value in a 17 kOe field equals to 5.0 J/kg*K for the GdFeSi compound and decreases sharply for the substituted compounds.

Acknowledgments
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